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Mesoporous V-AlPO – New Partial Oxidation Catalyst

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Abstract

Vanadium incorporated hexagonal mesoporous aluminophosphate characteristic of MCM-41 has been synthesized. Characterization of the catalyst has been done by using low angle XRD, N_2 adsorption, UV-VIS DRS, thermal analysis, XPS and ESR spectroscopy. These techniques confirm the presence of vanadium in both +4 and +5 oxidation states in the calcined material. Liquid phase partial oxidation of toluene has been carried out on V-AlPO using 70% TBHP and 30% H_2O_2 as oxidants. When 70% TBHP is used as an oxidant, it resulted in side chain oxidation giving rise to aldehyde/acid where as with 30% H_2O_2, side chain as well as ring oxidation takes place. Catalytic activity of V-AlPO has been compared with that of V-MCM-48 and other vanadium containing catalytic systems. It has been observed that mesoporous V-AlPO shows higher conversion and is also selective towards side chain oxidation products. The higher conversion of V-AlPO over V-MCM-48 has been attributed to the stabilization of the active $V^{+5/+4}$ species in AlPO framework as compared to silicate analogue.

Introduction

Catalytic oxidation of hydrocarbons in general is employed in the manufacture of fine chemicals. For the oxidation of aromatic hydrocarbons, homogeneous catalysts like sulfuric acid, various transition metal salts and phosphoric acid have been used [1,2]. However, solid catalysts like microporous aluminosilicates and aluminophosphates exhibit several advantages when compared to their homogeneous counterparts, *e.g.* ease of recovery, recycling and amenability to continuous processing [3]. The success of TS-1, a microporous titanosilicate, where titanium was isomorphously substituted into the framework of silica provoked a spate of activity in the development and application of redox molecular sieves containing metal ions other than titanium in organic synthesis [4]. Other than TS-1, VS-1, ZrS-1 and SnS-1 have been used for the oxidation of toluene [5-7]. Transition metal substituted Aluminophosphates like V-AlPO, Cr-AlPO have also been used as catalysts for the oxidation of aromatic substrates [8,9]. Though these microporous catalysts are active for the oxidation of toluene, the pore sizes of these materials limit their applications. With the recent discovery of mesoporous materials, the activity of transition metal containing MCM-41, MCM-48, HMS has been tested for the oxidation of alkylbenzenes with peroxides as oxidants [10,11]. But little attention has been paid to synthesize mesoporous aluminophosphates. Among the successful attempts, Si, Ti and Mn, Cr and V- have been incorporated into the framework of hexagonal mesoporous aluminophosphates and the resulting systems are active for various catalytic processes [12-17]. The present communication deals with the synthesis of V-analogues of mesoporous aluminophosphates via surfactant based hydrothermal method. The catalytic activity was tested for the partial oxidation of toluene with 70% tertiary butyl hydroperoxide (TBHP) and 30% hydrogen peroxide (H_2O_2) as oxidants and the activity was compared with that of V-MCM-48, V-MCM-41 and other reported systems.

Experimental

Synthesis of V-AlPO

Mesoporous vanadoaluminophosphate was prepared using cetyltrimethylammonium bromide (CTAB) as surfactant and with the following gel composition. $Al_2O_3 : xP_2O_5 : yV_2O_5 : zCTAB : TMAOH : wH_2O$, where x = 2.0-2.5, y = 0.01-0.2, z = 0.4-0.5 and w = 300-350. Various sources of aluminium have been tried and aluminium hydroxide has been chosen

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*corresponding authors. E-mail: bviswanathan@hotmail.com as the source. The pH of the gel was maintained at 9.5 with tetramethylammonium hydroxide (TMAOH), as the use of other sources like NaOH and NH_4OH led only to amorphous materials. The resulting gel was aged at room temperature for 3h followed by autoclaving at 423 K for 24 h. The solid was filtered, washed several times with deionised water and calcined at 773 K for six hours to remove the organic template.

Synthesis of mesoporous V-MCM-48

Sodium hydroxide was added to an aqueous solution of cetyltrimethylammonium bromide (CTAB) and stirred for 30 min. To this tetraethylorthosilicate and aqueous solution of vanadyl acetylacetonate was added. The resulting homogeneous gel was found to have the composition $SiO_2:V_xO_y:CTAB:Na_2O:EtOH:H_2O = 2.0:0.015:0.24:0.5:5.0:195$. The gel was stirred for 3 h at room temperature, and autoclaved at 423 K for 10 h. Filtration followed by calcination at 823 K for 6 h resulted in the formation of V-MCM-48.

Characterization

Various techniques have been used for the characterization of the materials synthesized. The low angle X-ray diffraction pattern of the sample was recorded on a Siemens D 500 ($\theta/2\theta$) using monochromatic Cu K_α radiation ($\lambda = 1.5406$ Å) with a scan speed of 1°/min over the range $2 < 2\theta < 10°$. Thermal analyses of the samples were made with thermal analyser (Perkin Elmer model TGA 7) at a heating rate of 20 °C/min. Diffuse reflectance UV-VIS spectra were recorded on a Cary 5 E UV-VISNIR spectrophotometer. ESR spectra were recorded with Varian E–112 spectrometer at room temperature. N_2 adsorption–desorption measurements at 77 K were made using CE instruments, Sorptomatic 1990. The sample was out gassed at 473 K for 12 h. X-ray photoelectron spectroscopic measurements (XPS) were performed on a PHI-550 ESCA-System (Perkin-Elmer GmbH).

Catalytic activity

Oxidation of toluene over V-AlPO and V-MCM-48 was carried out at 333K in a three necked round bottomed flask under reflux conditions using 70% TBHP as oxidant. Acetonitrile was used as a solvent. After each experiment the catalyst was filtered and dried. The dried catalysts were then calcined in air at 673 K for 6 h and reused. The results were compared with those reported in literature. The same reaction was carried out using 30% H_2O_2 as oxidant and acetonitrile as solvent. After each experiment, XRD was recorded to examine the morphological changes in the catalyst. The reaction products were identified by GC-MS (Hewlett-Packard, HPG 1800A GCD system, HP-5) and analysed by gas chromatograph (Shimadzu GC-14A, 30m HP-5. FID).

Results and discussion

XRD

The XRD pattern of V-AlPO is shown in Fig.1. XRD pattern shows a prominent peak corresponding to (100) reflection followed by weaker but clear peaks corresponding to (110) and (200) reflections, which can be indexed to a hexagonal lattice similar to MCM-41. After calcination, slight decrease in d_{100} was observed; this could be due to structural contraction during calcination processes. Tetramethylammonium hydroxide was used as a base for the synthesis of aluminophosphates. However, the use of NaOH and NH_4OH resulted in amorphous materials. The function of organic base is to modify the electrostatic interaction and thereby the formation of a weak ion pairs (I^-----TMA^+). If NaOH is used the Na^+ ions with a small ionic radius than TMA^+ has stronger ion-pair interaction with the aluminophosphate species and thereby preventing sufficient interaction with the cationic assembly [18].

XRD patterns of the MCM-48 materials are shown in Fig. 2. It can be seen that ordered MCM-48 mesoporous materials consistent with an *Ia3d* cubic symmetry were obtained. In this approach, MCM-48 materials have been synthesised at lower concentrations of the template. V-MCM-48 shows a maximum intense peak corresponding to (211) with a d-spacing value of 35.30 Å, which upon calcination decreased to 33.40 Å indicating the contraction of the structure during calcination. In addition to (211), these materials exhibit less intense peaks corresponding to (220), (321) and (400) reflections [19].

N_2 adsorption

N_2 adsorption-desorption isotherms of V-AlPO and V-MCM-48 are shown in Fig. 3. In the case V-AlPO, N_2 adsorption isotherms are of type IV with a small hysterisis loop characteristic of mesoporous ma-

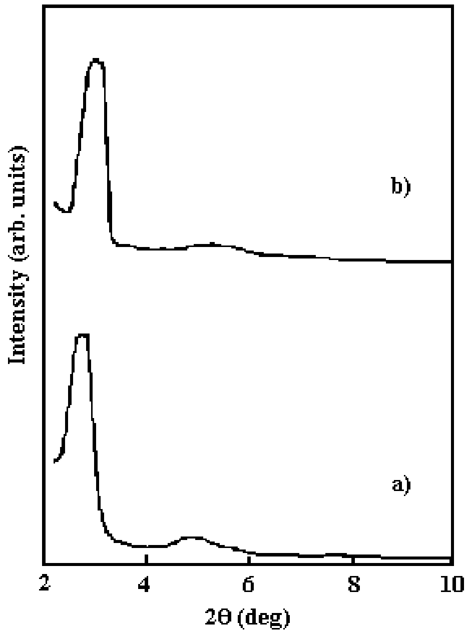

Fig. 1. XRD pattern of V-AlPO (a) uncalcined (b) calcined.

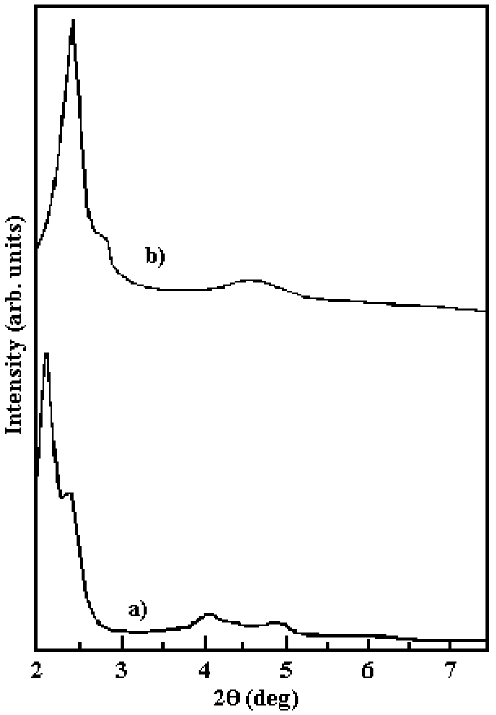

Fig. 2. XRD pattern of V-MCM-48 (a) uncalcined (b) calcined.

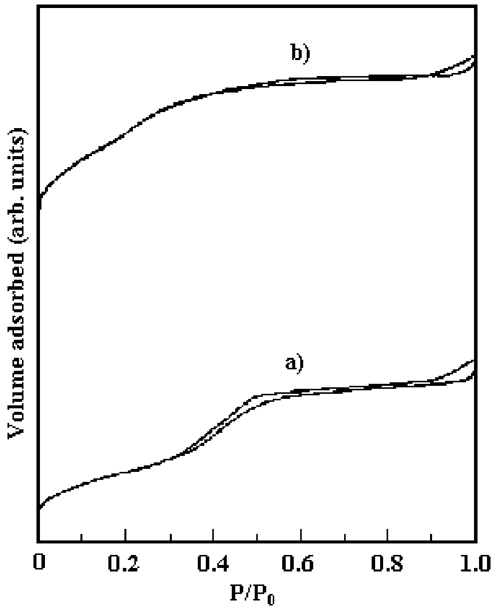

Fig. 3. N_2 adsorption-desorption isotherms of (a) V-MCM-48 (b) V-AlPO.

terials. The isotherms have an inflection around p/p_o = 0.2-0.3 indicative of mesoporous nature. The BET surface area is ~ 650 m^2/g, with an average pore size distributed around 29 Å.

The N_2 adsorption-desorption isotherms for V-MCM-48 are also of type IV. The isotherms also have an inflection around p/p_o = 0.2-0.3 indicative of mesoporous materials. BET surface area of V-MCM-48 is ~ 850 m^2/g and average pore size is 28 Å.

ESR spectroscopy

The ESR spectra of as synthesised and calcined AlPO are shown in Fig. 4. The ESR spectrum of as synthesised material, which originated from the d^1 electron interaction with nuclear spin (I_n= 7/2) of ^{51}V. The ESR parameters ($g_{\|}$= 1.948, $g_{\perp}$= 1.991, $A_{\|}$ = 191G and $A_{\perp}$= 65 G) indicate the presence of V^{+4} in distorted O_h environment [20]. Upon calcination, the signal intensity decreased with increase in the sharpness. This could be due to partial conversion of V^{+4} to V^{+5} during calcination. This is further supported by XPS studies.

XPS studies

The XPS spectrum of calcined V-ALPO in V2p region (515-518 eV) shown in Fig.5 indicates two peaks: one corresponding to V^{+4} at 516 eV and other one corresponding to V^{+5} at 517.4 eV. This confirms our contention that during calcination partial oxidation of vanadium takes place. XPS in combination with ESR data confirm the presence both +4 and +5 oxidation states of vanadium.

Catalytic activity

The oxidation of toluene with 70% TBHP over V-AlPO and V-MCM-48 has been carried out with

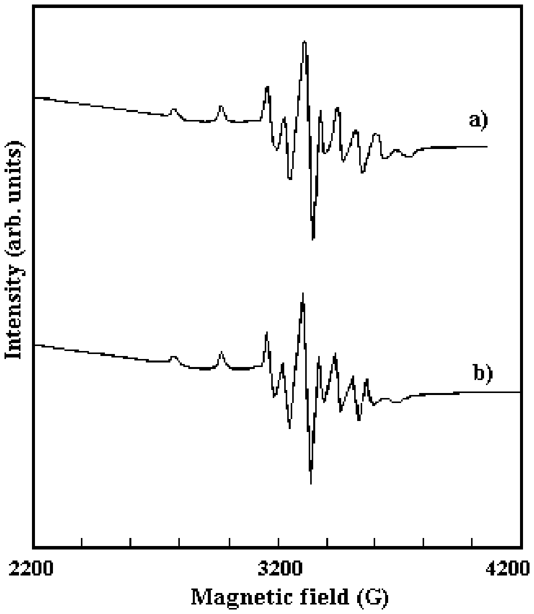

Fig. 4. ESR spectra of V-AlPO (a) uncalcined (b) calcined.

acetonitrile as a solvent. The results obtained are compared with various heterogeneous catalytic systems and are summarized in Table 1. Though VAPO-31 has higher conversion (44%), the selectivity to side chain oxidation product is less compared to mesoporous materials. The oxidation of toluene over mesoporous catalysts produced benzaldehyde/acid and benzyl alcohol with high selectivity towards aldehyde/acid (up to 97%). Interestingly, under the reaction conditions employed for the oxidation of toluene with TBHP, it was observed that both V-AlPO as well as V-MCM-48 have not produced detectable amounts of cresols indicating that these catalysts are promising side chain oxidation catalysts. Among mesoporous catalysts, V-AlPO has shown a slightly higher conversion and selectivity over aluminosilicate analogue. This could be due to the higher dispersion of active species in mesoporous aluminophosphate network.

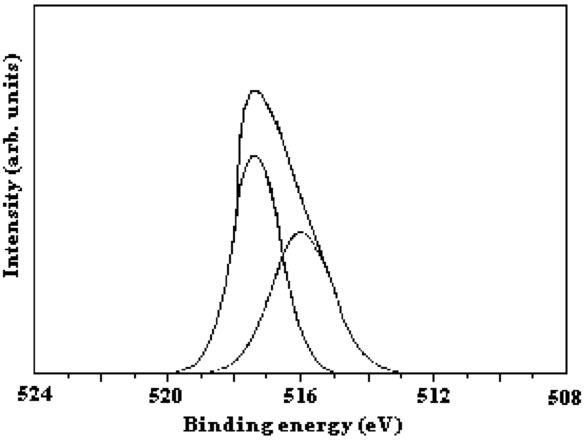

Fig. 5. XPS of V-AlPO (calcined).

The data on the comparative activity of various catalytic systems for the oxidation of toluene with 30% H_2O_2 in acetonitrile are given in Table 2. Though homogeneous catalysts show higher activity for toluene oxidation, their selectivity is higher for ring oxidation giving cresols as major products. However, heterogeneous catalysts show higher selectivity to side chain oxidation giving aldehyde/acid and al-

Table 1

Performance of various catalysts for oxidation of toluene with 70% TBHP

Catalyst	Temp (K)	Conv. of Toluene (%)	Product selectivity (%)			
			(o/p) cresols	Benzaldehyde/acid	Benzylalcohol	Others
VAPO-31	303	44.0	---	65.0	6.0	29.0
V-ALPO[a]	333	21.5	---	96.1	3.9	--
V-MCM-48[a]	333	19.4	---	94.5	2.5	3.0
Cr-S-1 [21]	353	18.4	0.7	28.5	25.7	45.1[#]
VAPO-5 [6]	343	13.0	---	89.0	5.0	6.0
VS-1 [5]	353	8.3	8.0	58.0	24.8	---
Cr/S-1 [22]	353	3.3	5.6	57.4	37.0	---
Blank [22]	353	2.1	---	>99	---	---

Reaction conditions: weight of the catalyst = 100 mg, solvent --- acetonitrile, reaction duration (t) = 24 h

[a] reaction duration --- 6 h

[#] -- dibenzyl

cohol. Under the reaction conditions employed, among heterogeneous catalysts, V-AlPO exhibit higher conversion (28.4%) with higher selectivity (~78%) to side chain oxidation products.

Table 2

Performance of various catalysts for oxidation of toluene with 30 % H_2O_2

Catalyst	Temp (K)	Conv. Of Toluene (%)	Product selectivity (%)			
			(o/p) cresols	Benzaldehyde/acid	Benzyl alcohol	Others
V-ALPO[a]	333	28.4	21.8	73.2	4.0	1.0
V-MCM-48[a]	333	22.7	25.5	68.5	1.5	4.0
V-MCM-41[a] [23]	333	20.8	34.0	62.0	2.0	2.0
V-Al-Beta[a] [24]	333	14.0	38.0	56.0	4.0	2.0
VS-2[a] [25]	333	11.7	36.8	52.2	7.7	3.7
Vanado peroxo complex [26]	303	52.0	96.2	3.8	--	---
$H_4PVMo_{11}O_{40}$ [27]	303	21.6	89.2	10.1	<1	--
$H_5PV_2Mo_{10}O_{40}$	303	25.6	91.5	7.7	<1	--
$H_6PV_3Mo_9O_{40}$	303	48.3	91.6	8.4	--	--
$H_5PV_2Mo_{10}O_{40}$	331	35.4	91.4	8.6	--	--

Reaction conditions: weight of the catalyst = 100 mg; solvent –acetonitrile, duration of the reaction (t) = 3 h
[a]duration of the reaction (t) = 18 h

Conclusions

Even though vanadium peroxo complex is a well-known oxidation catalyst for nearly four decades or more, it is possible now to make use of vanadium (+5/+4) in controlled environments to carryout selective oxidation by proper choice of the oxidant. It is possible to design catalyst systems, which can provide selectivity greater than 80%. It is presumed that these catalytic systems will soon be exploited for commercial operations.

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